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A COMPARISON OF QUARTZ CRYSTAL MICROBALANCE MEASUREMENTS WITH MASS SPECTROMETER DETERMINATIONS

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ABSTRACT

An experimental program has been undertaken in which mass accretion rates, as determined by a liquid nitrogen cooled quartz crystal microbalance, were compared with the mass flux rates, as determined by both a cycloidal type and a quadrupole type residual gas analyzer for five simple materials. The data indicate a high degree of correlation between these instruments insofar as the shape of the curves. There are large variations however among the absolute values. These differences are probably due in the main to uncertainties in the sensitivities of the residual gas analyzers to materials tested.

INTRODUCTION

The quartz crystal microbalance (QCM) is basically a mass measuring device. It can be used to measure mass flux by determining the mass difference due to accretion over a known time interval. Knowing the temperature and molecular weight of the particles impinging on and adhering to the QCM, one may convert the flux measurements to pressure.

The residual gas analyzer (RGA), such as either of the two used in this study, is basically a number density sensitive device. Assuming a known temperature for the molecule, this then can be used as a pressure measuring device. The pressure measurement may be translated into a mass flux measurement of the instrument identified molecular species.

Therefore, by applying the factors involving the temperature and molecular weight of the material under study, the data from the RGA should therefore be directly comparable with the QCM data. Furthermore, if the RGA data are left in terms of pressure, they should bear a relation to the QCM mass flux data which is a function of the square root of the molecular weight of the material.

This experimental program was undertaken to test these hypotheses.

Theory

The theory behind operation of an RGA is well explained in a number of sources (References 1 and 2). Two types of instrument were used in this investigation. One was a Consolidated Engineering Corp. Model 21-614 cycloidal focusing mass spectrometer. In this instrument, ions are formed by the impact of electrons upon a representative molecular density in an ionizer section. These ions are accelerated, focused, and then dispersed. The dispersion of the ions is a function of the mass-to-charge ratio (m/e) and is caused by crossed magnetic and electrostatic fields. Varying the electrostatic field, E , while maintaining a constant ratio of E to the accelerating potential, causes a scanning of the ions of the various m/e ratios past a slit to a detector. The value of the ion current, measured through an electron multiplier, is a function of the number of impacting ions and in this way one may establish a relationship between the ion current (nominally, a partial pressure) and the particular value of m/e corresponding to the magnitude of E at that time.

The second instrument was of the quadrupole type and was manufactured for Goddard Space Flight Center in 1965 by Bell and Howell Co., Pasadena, Cal. In this type of instrument, ions are formed from the ambient molecules as in the case of the cycloidal RGA. Separation of the ions of varying m/e ratios however is accomplished in an electric field consisting of a direct current and a radio frequency field. The ions follow paths described by the Mathieu equation. Only ions with the proper m/e ratio (as selected by the strength and frequency of the electric fields created by the four rods) pass through the field of the detector. Here again, an electron multiplier is used to amplify the ion current.

Both of these devices basically measure number density, n . Assuming the temperature, T , to be constant for all the molecules, the RGA can be considered to measure pressure, P , as

$$P = nkT \quad (1)$$

where k is the Boltzman constant.

The theory of the quartz crystal microbalance, too, is well defined in the literature (References 3, 4 and 5). The instrument is basically a quartz crystal oscillating in the shear mode. The shear mode resonant frequency of the quartz crystal is given by

$$f = \frac{c}{2t} = \frac{N}{t} \quad (2)$$

where c is the velocity of the transverse wave in the direction of thickness t . Differentiating this expression with respect to the thickness and assuming that accumulation of mass dm on the crystal of area A and crystal density ρ is equivalent to a change of crystal thickness dt , i.e., $dt = dm/\rho A$, one obtains

$$df = -\frac{1}{N\rho A} f^2 dm = -\frac{f}{t\rho A} dm = -C_f \frac{dm}{A} \quad (\text{Hz} \cdot \text{g}^{-1}). \quad (3)$$

The mass sensitivity, C_f , is $2.22 \times 10^8 \text{ Hz} \cdot \text{cm}^2 \cdot \text{g}^{-1}$ for a crystal of thickness $t = 1.7 \times 10^{-2} \text{ cm}$, density, $\rho = 2.65 \text{ g} \cdot \text{cm}^{-3}$ and resonant frequency, $f = 10 \times 10^6 \text{ Hz}$.

The change of frequency with time, \dot{f} , resulting from the accretion of mass per unit time, \dot{m} , will be

$$\dot{f} = -c_f \frac{\dot{m}}{A} = -c_f \nu \frac{M}{N_0} = c_f \phi \quad (\text{Hz} \cdot \text{s}^{-1}) \quad (4)$$

where M is the molar mass, $\text{g} \cdot \text{mole}^{-1}$, of the gas, N_0 is Avogadro's number, ν is the molecular flux and ϕ , the mass accretion rate. The rate of mass accretion can be expressed as a function of the gas pressure P ($\text{N} \cdot \text{m}^{-2}$), the gas temperature T (degrees K) and the molar mass, M . Therefore, one may write:

$$\phi = \frac{PM}{4RT} \left(\frac{8RT}{\pi M} \right)^{1/2} = \frac{5.83 \times 10^2}{133} \sqrt{\frac{M}{T}} P \quad (\text{g} \cdot \text{cm}^{-2} \text{ s}^{-1}). \quad (5)$$

where: R = gas constant

The frequency change in this form will be

$$\dot{f} = -c_f(\phi) = -c_f \left(4.38 \times 10^{-4} \sqrt{\frac{M}{T}} \right) P \gamma = -k_f P. \quad (6)$$

A coefficient γ has been introduced to account for the actual amount of the impinging mass flux which is retained by the crystal. The coefficient is the condensation or the sticking coefficient depending on whether the molecules condense on molecules of the same species or on a different substrate. For condensation on the same material, the coefficient will be a function of the gas, gas temperature, and crystal temperature. For cryogenic crystal temperature and gas temperature less than 300K, the

coefficient varies from about 0.1 to 1.0 for common gases. Of the materials used in this study, the value for water was found to be 0.9 at 77K (Reference 10). The values for the other materials were not available.

The quartz oscillator can be used as a pressure indicator when the constant $K_f = c_f \gamma \cdot 4.38 \times 10^{-4} \sqrt{M/T}$ ($\text{Hz} \cdot \text{s}^{-1} \cdot \text{N}^{-1} \cdot \text{m}^2$) is evaluated for each gas. It is also apparent that the condensation coefficient could be evaluated if one compares the mass flux measured by the quartz oscillator to the impinging flux since

$$\gamma = \frac{\phi}{\phi_i} = \frac{\dot{f}/c_f}{\phi_i} = \frac{\dot{f}/c_f}{4.38 \times 10^{-4} \sqrt{M/T} P_i} \quad (7)$$

where the subscript i indicates the impinging flux. In regard to the response of the quartz oscillator as a function of the mass accretion, substitution of $f = f - \Delta f$ in equation (3), and disregarding high order values of Δf one obtains

$$\frac{df}{dm} = -\frac{1}{N\rho A} f (f - 2\Delta f) = -\frac{c_f}{Af^2} f(f - 2\Delta f). \quad (8)$$

This indicates that the frequency shift is not linearly related to the change of mass accretion. The deviation from linearity is given by

$$D = \frac{f_i^2 - f_i (f_i - 2\Delta f)}{f_i^2}. \quad (9)$$

It can be shown that linearity is maintained if one measures the period change ($1/f$) instead of frequency change. In this report, since the data was recorded in terms of frequency, the correction indicated by equation (9) has been applied assuming that the crystals have a natural frequency of 1×10^7 Hz. The flux accretion was then, from equation (8) found to be

$$\frac{\Delta M}{A\Delta t} = \phi_M = \frac{N\rho \left(\frac{f_2 - f_1}{\Delta t} \right)}{(f_0 + f_1) [(f_0 + f_1) - 2(f_2 - f_1)]} (\text{g} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}) \quad (10)$$

where:

ρ = density of quartz, $\text{g} \cdot \text{cm}^{-3}$

Δt = time interval over which the measurements were made, 100 s

f_1 = initial beat frequency, Hz

f_2 = final beat frequency, Hz

f_0 = estimated natural, unloaded frequency, Hz.

Assuming both the two RGA's and the QCM to have a response which is linear with number density and accreted flux respectively, one would expect that by comparing one with the other, the data should fit a first degree equation. Curves of the form $y = mx + b$ and $y = ax^d$ were fitted to the data. Least square solutions as found in References 6 and 7 were applied to the data. These also permitted an evaluation of the goodness of fit in the form of a correlation coefficient, r , which may range from zero, indicating no correlations, to ± 1 , indicating perfect correlation.

In addition, the RGA flux readings may be converted into pressure by the equation

$$P = G \left(\frac{M}{T} \right)^{-1/2} \phi \quad (11)$$

where

G = a coefficient which includes units conversion ($.228 \times 10^{-4}$),

Assuming the gases coming to either of the RGA's or to the QCM to be at room temperature (298K), the equation then becomes:

$$P = 3.93 \times 10^4 (M)^{-1/2} \phi \quad (12)$$

where: $G\sqrt{T} = 3.93 \times 10^4$

For any given M , we then have a first degree equation between P and ϕ and one should be able to compare P as found by the RGA with ϕ as found by the QCM.

For the remainder of this report, the subscript RGA will refer to values obtained by either of the two residual gas analyzers, subscript C will indicate the cycloidal RGA and subscript Q the quadrupole RGA. The

subscript M will refer to measurements made by the quartz crystal microbalance. Also, ϕ will be used to indicate flux in $\text{g} \cdot \text{cm}^{-2} \text{ s}^{-1}$ and P will be used to indicate pressure in $\text{N} \cdot \text{m}^{-2}$.

Test Configuration

Figure 1 shows the chamber in which this investigation was conducted. The 36 cm (14 inch) glass bell jar which completes the system is removed so that the QCM may be seen. The system is pumped via two elbows by two 15 cm liquid nitrogen (LN_2) trapped oil diffusion pumps. The relative location of the various instruments can be seen. The RGA's have been previously described.

Figure 2 is a photograph of the QCM configuration. The system basically consisted of an LN_2 cooled mounting block on which were mounted two mounting rings. To these rings were attached the quartz crystals. The crystals were edge mounted using a polyurethane adhesive (Dupont L-100 urethane with Dupont MOCA polymerizing agent using tetrahydrofuran as a vehicle).

The crystals used were 1.27 cm in diameter, AT cut at $39^\circ 49'$, and 1.7×10^{-2} cm thick to have a natural frequency of 10 MHz. Only the active crystal can be seen in Figure 2. The reference crystal is mounted similarly to a mounting ring and is between the active crystal and the mounting block. The reference crystal and the rear of the active crystal are vented to the chamber by means of a groove milled into the mounting ring. The groove is made with a right angle in it so that, when cooled by the LN_2 , it forms an effective baffle to contaminants. The beat frequency of the two crystals was read on a Hewlett-Packard 3735A frequency counter at ten second intervals over a period of 100 seconds (to insure stability of the readings).

The Bell and Howell quadrupole RGA output was read on a Mark 280 Brush recorder and the CEC 21-613 cycloidal RGA on a Leeds and Northrup Speedo-Max G recorder.

Test Procedure

The general test procedure was to close the leak valve and fill the sample holder (see Figure 1) which was a copper tube about 15 cm long and 0.6 cm in diameter with a few cubic centimeters of the sample liquid. The sample holder was then attached to the inlet system via a flexible plastic hose. The holder was then immersed in LN_2 to solidify the liquid and achieve a very low vapor pressure. The inlet system was then roughed out with an auxiliary mechanical roughing pump. After roughing, the valve to the roughing line was closed and the leak valve was opened to the previously evacuated chamber. The leak valve was then closed and LN_2 admitted to the QCM.

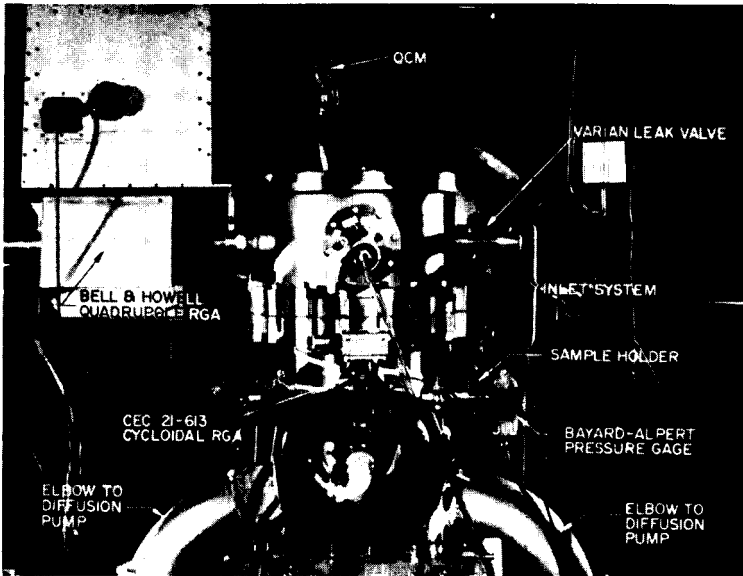


Figure 1. Test Configuration

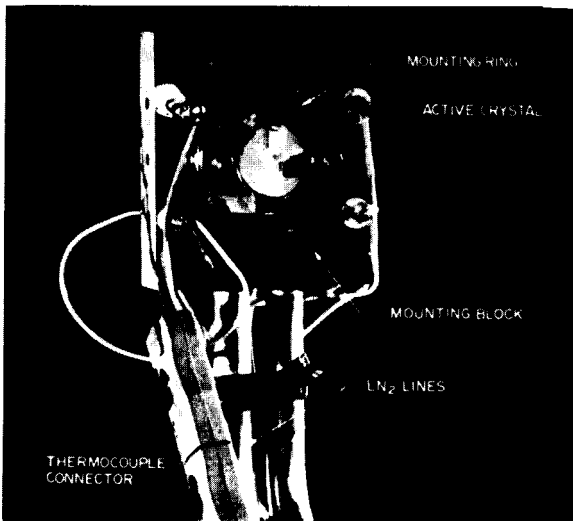


Figure 2. QCM Configuration

After reaching a steady state as noted by the Bayard-Alpert ionization gage, the RGA's, and a steady, slow accretion rate as noted on the QCM (usually in the order of $1/2 \text{ Hz} \cdot \text{s}^{-1}$), background measurements were made. The condensable component, as measured with the RGA, was substantially all water. Pressure, as measured by the ionization gage was typically about $1.5 \times 10^{-5} \text{ N} \cdot \text{m}^{-2}$ of which water formed about 76%, nitrogen 18%, oxygen 4%, and carbon dioxide 2%. The leak valve was then opened until the pressure, as measured on the ionization gage, roughly doubled. Stability was again established and the instrument readings recorded. This doubling procedure was continued until the accretion rate increased so rapidly as to cause the change in frequency over the period of the test to exceed 50 KHz or the RGA outputs to become saturated.

At the completion of the test, the LN_2 supply to the QCM was stopped and the crystals allowed to warm up releasing the accreted mass before the next material was admitted. In most cases, the chamber was opened between runs.

The five materials used in this investigation were:

1. Water, H_2O , molecular weight = 18.
2. Ethanol, $\text{CH}_3\text{CH}_2\text{OH}$, molecular weight = 46
3. Benzene, C_6H_6 , molecular weight = 78
4. Xylene, C_8H_{10} , molecular weight = 106
5. Carbon Tetrachloride, CCl_4 , molecular weight = 152

Data Reduction

The basic test data took three forms: QCM data was recorded as a beat frequency (Hz) at given time intervals, the cycloidal RGA data was read from a chart and was recorded as divisions, and the quadrupole data was read from a chart as amperes.

Using equation (10), the QCM data was interpreted as the mass flux of that material impinging on and sticking to the QCM ($\text{g} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$). Except in the case of water, the background flux was subtracted from each reading. This leaves a net ϕ_M which is due to the test material only. Since the condensable background is mostly water, this subtraction was not performed on the water data.

In order to utilize the RGA data, it was necessary to conduct a calibration of the RGA's against the ionization gage using nitrogen as the medium. The ionization gage was, in turn, calibrated in a small in-house calibration facility which uses a Baratron pressure gage as a working standard on the high pressure side of a two stage orifice system. The system is basically calibrated with a McCloud gage.

Given a calibration of the RGA for nitrogen, a major difficulty arose in the calibration for the materials undergoing test. For water

and benzene the sensitivities from Reference 8 were used; the sensitivities for the other materials were taken from Reference 9. These, however, are given with respect to n-butane and therefore the sensitivity for n-butane with respect to nitrogen must be accounted for. This value was taken from Reference 8.

Another difficulty arises from the fact that the sensitivities found in Reference 9 are the result of the works of a number of laboratories. Each laboratory report is denoted by a serial number in Reference 9. It is found that results by different laboratories for the same material vary considerably. For instance, the sensitivity for xylene (taken as 1,2-dimethylbenzene) are found in ser. no. 178 as 0.87 and 0.91. Data from ser. no. 307, another laboratory, is found to be 1.41, different by almost a factor of two. In this investigation, prime reliance was placed in the data from Reference 8 since this was from the manufacturer of one of the RGA's being used. Other sensitivities were taken as the average of source found in Reference 9 excluding any data which was significantly different from the other sources.

Table I below shows the sensitivities used and the sources.

Table I
RGA Sensitivity Values

Material	Sensitivity with Respect to:	
	n-Butane, S_B	Nitrogen, S_N
n-Butane	-	0.85 (Reference 8)
Water	-	1.3 (Reference 8)
Ethanol	0.63 (Reference 9, ser. nos. 364, 1620, and 1646)	1.3 *
Benzene	-	0.63 (Reference 8)
Xylene	0.89 (Reference 9, ser. no. 178)	0.96 *
Carbon Tetrachloride	0.38 (Reference 9, ser. no. 603)	2.2 *

$$*S_N = \frac{S_N \text{ for n-Butane}}{S_B}$$

Tests run to determine the sensitivity of the RGA's for nitrogen C_{RGA} , indicated that the sensitivity of the cycloidal RGA was 2.39×10^{-8} ($N \cdot m^{-2} \cdot Division^{-1}$) and the quadrupole RGA was 1.45×10^6 ($N \cdot m^{-2} \cdot Amper^{-1}$). These figures were corrected by the gage calibration, C_1 , found to be 0.89. The typical calculation was then of the form

$$P_{\text{RGA}} = (\text{Instrument Divisions or Amperes}) (C_{\text{RGA}}) (C_1) (S_N) \quad (13)$$

and then the flux, ϕ_{RGA} , equals

$$\phi_{\text{RGA}} = P_{\text{RGA}} \left[4.38 \times 10^{-4} \left(\frac{M}{T} \right)^{1/2} \right]. \quad (14)$$

Data Analysis

Using the relationships established in the previous section, values were obtained for ϕ_M , ϕ_C , and ϕ_Q . Since these are also related to the pressure as a function of the square root of the molecular weight, relationships of ϕ_M with P_C and P_Q were also established.

As noted earlier, it was expected that the two instruments would be linearly related. Curves of the form $y = mx + b$ and $y = ax^d$ were fitted to the data; the exponential form was tried to investigate the variation from a first degree equation. Table II presents the equations for the various substances. The correlation coefficients in all cases were greater than 0.998.

Table II
RGA Pressure as a Function of Quartz Crystal
Microbalance Measured Flux

Material	$P_{\text{RGA}} = m\phi_M + b$	$P_{\text{RGA}} = a\phi_M^d$
Water:	$P_T = 9263 \phi^*$ $P_C = 5670 \phi_M + 1.72 \times 10^{-5}$ $P_Q = 5130 \phi_M + 6.80 \times 10^{-6}$	$P_C = 3640 \phi_M^{0.970}$ $P_Q = 3480 \phi_M^{0.976}$
Ethanol:	$P_T = 5794 \phi^*$ $P_C = 4700 \phi_M + 1.08 \times 10^{-5}$ $P_Q = 7469 \phi_M + 4.05 \times 10^{-6}$	$P_C = 4130 \phi_M^{0.989}$ $P_Q = 5370 \phi_M^{0.980}$
Benzene:	$P_T = 4450 \phi^*$ $P_C = 3000 \phi_M - 3.04 \times 10^{-7}$ $P_Q = 3230 \phi_M - 3.45 \times 10^{-6}$	$P_C = 3430 \phi_M^{1.008}$ $P_Q = 3600 \phi_M^{1.010}$
Xylene:	$P_T = 3817 \phi^*$ $P_C = 3420 \phi_M - 1.53 \times 10^{-7}$ $P_Q = 4410 \phi_M + 1.34 \times 10^{-6}$	$P_C = 3470 \phi_M^{1.001}$ $P_Q = 3530 \phi_M^{0.986}$
Carbon Tetrachloride:	$P_T = 3167 \phi^*$ $P_C = 1460 \phi_M - 1.16 \times 10^{-6}$ $P_Q = 2250 \phi_M - 4.29 \times 10^{-6}$	$P_C = 2540 \phi_M^{1.034}$ $P_Q = 3180 \phi_M^{1.024}$

* P_T is what one would expect assuming an ideal case, e.g., condensation coefficient equals 1.0 and RGA sensitivities being perfect.

Figure 3 shows both equation forms plotted against the actual data points for water. The curves are rather typical of the data in that the power curve fit appears to the eye to be the better one. The line with a slope of 1, the ideal case, is placed in the figure as a reference. Figures 4 and 5 are plots of the data obtained with the RGA's, ϕ_C and ϕ_Q , against ϕ_M for all five materials. In all cases the slopes are near the expected value of 1.0 but their distance from the expected line varies with both instrument and material.

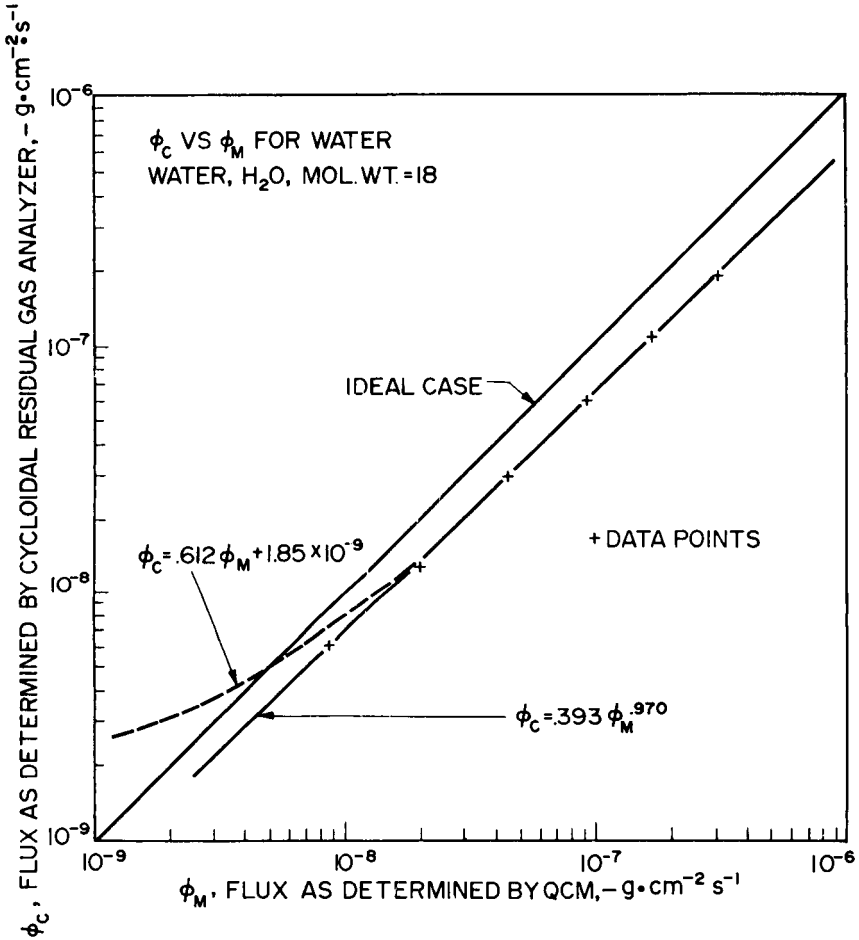


Figure 3

If this data is replotted as P_{RGA} vs ϕ_M for all materials, one would expect a family of curves with a slope of 1.0 and the position of the curve dependent on the molecular weight. This type of presentation is contained in Figures 6 and 7. In these figures the curves plotted are of the form $y = ax^d$. The materials and their molecular weights are shown

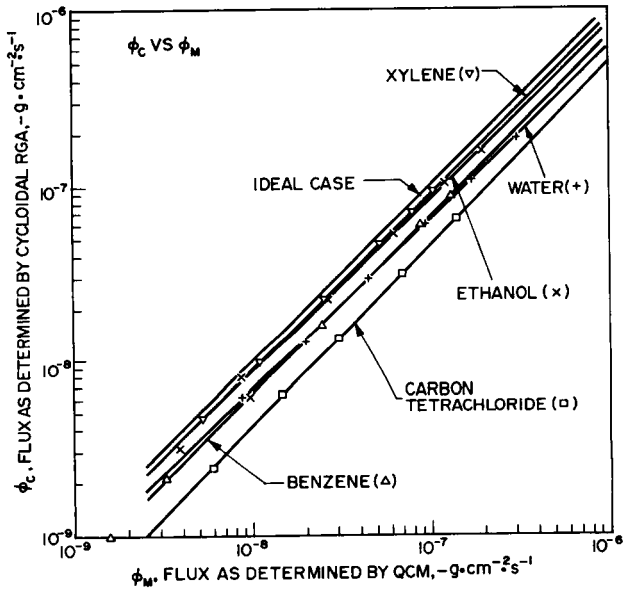


Figure 4

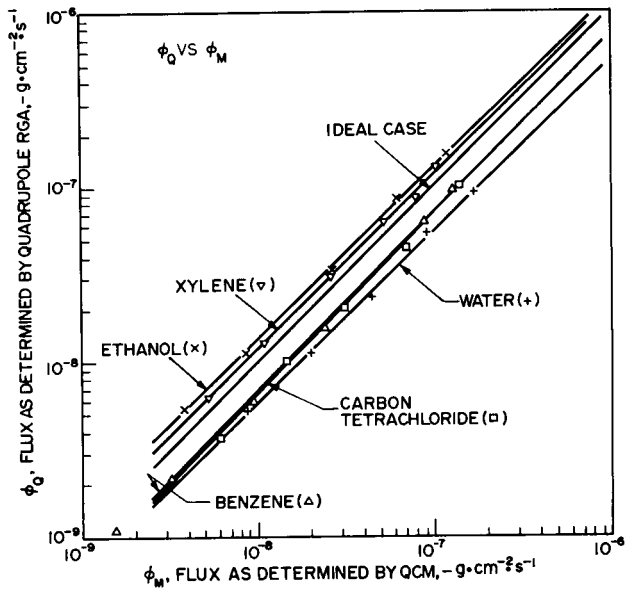


Figure 5

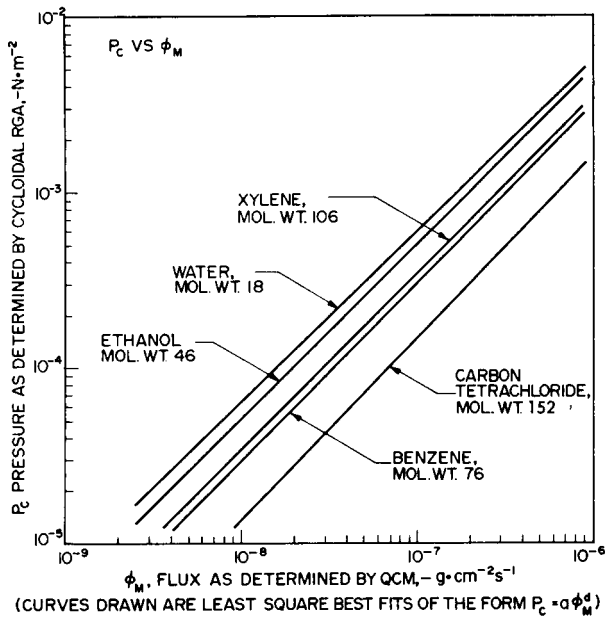


Figure 6

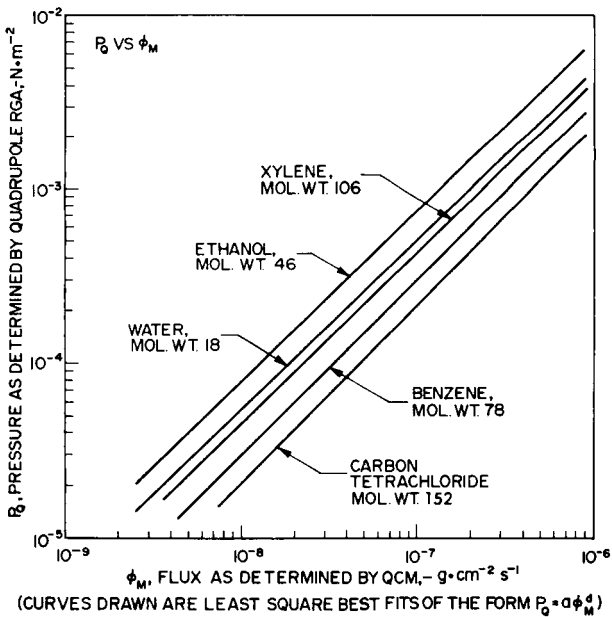


Figure 7

on the figures. It can be seen that they do not vary monotonically with molecular weight. For instance, in Figure 6 xylene and benzene seem to be out of sequence and in Figure 7 water and ethanol are also out of sequence.

A more readily apparent presentation is to be seen in Figures 8 and 9. In these, the coefficient of ϕ_M (a or m as the case may be) is plotted against M, the molecular weight. In addition, a line is drawn which expresses the expected theoretical result. This value is derived simply by assuming the linear relationship and writing pressure as a function of flux (see equation 12). The value a, or m, then is set as

$$a, \text{ or } m, = 39,300 (M)^{-1/2}. \quad (15)$$

In Figure 8, which is based on the form $P = a\phi^d$, water seems to be furthest from the expected value; in Figure 9, based on the form $P = m\phi + b$, there is significantly more scatter, with water and carbon tetrachloride being furthest from the expected value.

It is interesting to note that in the cases of water and benzene, the data from the two RGA's virtually lie one atop the other in Figures 8 and 9. (It might be noted that in these two cases the sensitivities were taken from Reference 8.) The other cases, except for ethanol on Figure 8, show a significant scatter. Two major questions arise. First, why do the points for the same material differ from each other for the two different RGA's, and second, why do they not lie on the predicted line?

In partial answer to the first, one can hypothesize that the two instruments do not have equal sensitivities for all materials. This would not be at all unexpected in view of the varying sensitivities reported by different investigators using rather similar analyzers. One would, however expect closer correlation between the way the analyzers act upon water and ethanol or upon benzene and xylene because these materials have certain chemical similarities as opposed to the fact that they seem to act the same way between water and benzene - chemically quite dissimilar.

As to the second question, we may again strongly suspect erroneous values for the assumed sensitivities. Figures 4 and 5 show that the major problem does not lie in the assumption of a condensation coefficient of 1.0 inasmuch as the data often indicates a coefficient greater than 10, an impossibility. The differences in instrument position might account for different fluxes at these locations but this should not be a function of the material.

Summary of Conclusions

First, the data supports the hypothesis that the QCM and RGA both act in a linear manner in the range of pressures investigated. Second, a

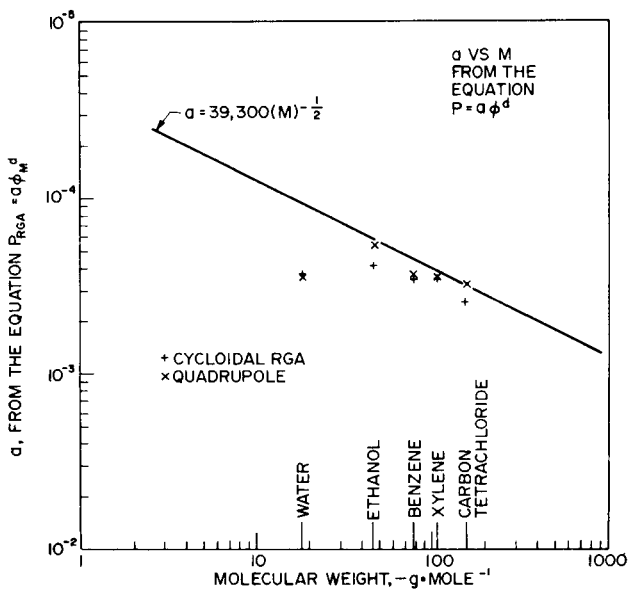


Figure 8

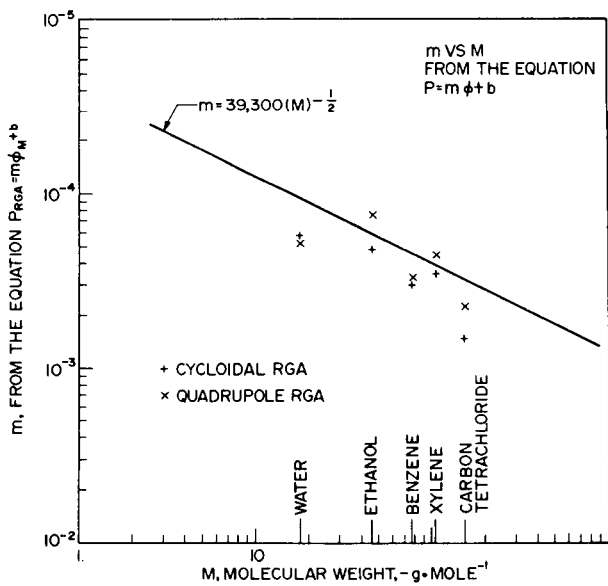


Figure 9

great uncertainty exists in the literature values of sensitivities for the RGA and this is reflected back as differences between fluxes measured by the QCM and fluxes, or pressures, measured by the RGA's. Water, traditionally a difficult substance to investigate, again appears to have the greatest uncertainties associated with the data. Third, while the data shown in Figures 8 and 9 do not follow the predictions, the general trend is there and, with proper sensitivities, would probably fit the predictions quite closely.

As a last item, the use of a QCM at cryogenic temperatures appears to be a viable method for obtaining sensitivities for mass spectrometers. If the condensation coefficients are known, this method should be quite accurate and would permit in-situ calibration of an RGA.

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*These references were obtained from the Hewlett-Packard Calculator Model 9100A Program Library, Program numbers 09100-70803 and 09100-70811.